

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-202408  
 (43)Date of publication of application : 19.07.2002

(51)Int.CI. G02B 5/30  
 G02F 1/13363

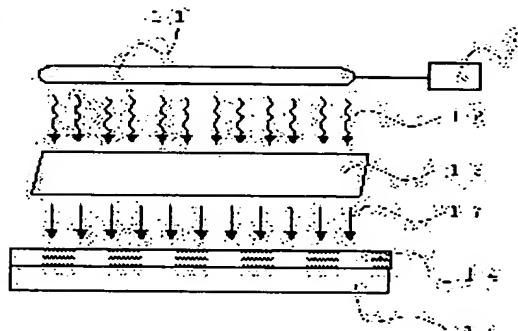
(21)Application number : 2000-400355 (71)Applicant : HAYASHI TELEMPU CO LTD  
 (22)Date of filing : 28.12.2000 (72)Inventor : SAKAI TAKEYA  
 UETSUKI MASAO  
 KAWATSUKI YOSHIHIRO

## (54) RETARDATION FILM AND METHOD FOR MANUFACTURING THE SAME

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To realize a retardation film having significant wavelength dispersion and temperature compensation effect to transmitted light and a controlled optical axis direction and a method for manufacturing the same by exposing and orienting in a molecular level a film of a mixture of a photosensitive polymer and a low molecular weight compound.

**SOLUTION:** The film of the mixture of the photosensitive polymer and the low molecular weight compound is formed. The retardation film having the significant wavelength dispersion and the temperature compensation effect toward the transmitted light is obtained by exposing the film using a device consisting of an ultraviolet lamp and a power source or an optical element transforming natural light to polarized light (e.g. a Glan-Taylor prism) and enhancing a photoreaction of photosensitive groups aligned in a specified direction. The optical axis is oriented with arbitrary inclination by carrying out the irradiation from a direction inclined with respect to the film surface. As a result, the retardation film having the significant wavelength dispersion and the temperature compensation effect toward the transmitted light and the optic axis set to a desired direction is provided.



### LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of  
rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

**\* NOTICES \***

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.

---

**CLAIMS**

---

**[Claim(s)]**

[Claim 1] While being produced at the process which includes the actuation which carries out an optical exposure in the film of a photosensitive polymer and the mixture of a low molecular weight compound The ratio (R80 degree-C/R30 degree C) of 30-degree C phase contrast and the phase contrast in 80 degrees C about the average wavelength field of the light by  $0.01 < R80 \text{ degree-C} / R30 \text{ degree-C} < 0.97$  The ratio (R400 nm/R550nm) of the phase contrast measured on the wavelength of 400nm and the phase contrast measured on the wavelength of 550nm is  $1.15 < R400 \text{ nm} / R550\text{nm}$ .

The phase contrast film characterized by the inclination (theta) of the optical axis measured by the crystal rotation method being  $0 \text{ degree} \leq \theta < 90 \text{ degrees}$ , and its manufacture approach.

[Claim 2] The phase contrast film of claim 1 characterized by being produced at the process which includes the actuation which carries out an optical exposure from front rear-face both directions in the film of a photosensitive polymer and the mixture of a low molecular weight compound, and its manufacture approach.

[Claim 3] The phase contrast film of claim 1 characterized by being produced at the process which includes the actuation which carries out an optical exposure from both directions on the back through a front face and a base material in the film of the photosensitive polymer formed on the base material, and the mixture of a low molecular weight compound, and its manufacture approach.

[Claim 4] The phase contrast film whose light irradiated in claim 1, claim 2, and claim 3 is linearly polarized light nature or partially polarized light nature, and its manufacture approach.

[Claim 5] The phase contrast film characterized by including the process heated and/or cooled in claim 1, claim 2, claim 3, a phase contrast film according to claim 4, and its manufacture approach, and its manufacture approach.

---

[Translation done.]

**\* NOTICES \***

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

---

**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** By what (henceforth exposure) ultraviolet rays are irradiated for at the film of a photosensitive polymer and the mixture of a low molecular weight compound, molecular orientation of this invention is carried out, and it relates to the phase contrast film which made big wavelength dispersion nature, the temperature-compensation effectiveness, and the direction of an optical axis discover at arbitration, and its manufacturing method. (Especially the phase contrast film with which the optical axis inclined to the film plane is effective in angle-of-visibility expansion in a liquid crystal display.)

**[0002]**

**[Description of the Prior Art]** A phase contrast film is required of black and white in the liquid crystal display of a STN mold, or colorization. This phase contrast film passes the linearly polarized light component which vibrates in the perpendicular direction of a main shaft mutually, and it is a film which has the birefringence which gives phase contrast required among these 2 components, and the ovality of the elliptically polarized light of R, G, and B which have penetrated the liquid crystal cell of a STN mold is decreased, or it enables [ rotates the main shaft of the elliptically polarized light of R, G, and B in the fixed direction, and ] black and white or colorization. As such a phase contrast film, polymeric materials, such as a polycarbonate, are extended, orientation of the macromolecule chain is carried out, and there are a refractive index of the extension direction and a thing which made the refractive index of the rectangular direction produce a difference to the extension direction. However, in order for the wavelength dispersion nature of a liquid crystal cell to become large since the big liquid crystal ingredient of a birefringence is used, and to compensate this with the liquid crystal display of which high-speed responsibility is required, a big phase contrast film of wavelength dispersion nature is desired. Moreover, since the retardation of a STN mold liquid crystal cell changes in connection with a temperature rise, when using a liquid crystal display as an object for mount, a color gap arises under an elevated temperature and a display property falls. This is for relaxation of the orientation of a liquid crystal molecule to arise by the rise of temperature in the liquid crystal cell of the liquid crystal display of a STN mold. Although the bilayer type STN mold liquid crystal display which used the liquid crystal cell for optical compensation can be considered to these technical problems, there are problems, like becoming [ which gains in the weight of a liquid crystal display ] thick, and cost becomes high. With the phase contrast film which extended polymeric materials, such as a polycarbonate, wavelength dispersion nature is small and an optical compensation effect is not fully acquired. As a large phase contrast film of wavelength dispersion nature, the phase contrast film which extended polymeric materials, such as polyarylate, polysulfone, polyether sulphone, and aromatic polyester, is mentioned. However, with the phase contrast film to which orientation of these macromolecules was carried out, relaxation of the molecular orientation under an elevated temperature is small, and when the retardation of the liquid crystal cell and phase contrast film which were adjusted as a room temperature showed the best display property separates from optimum conditions under an elevated temperature, an optical compensation effect is not fully acquired. Furthermore, with the phase contrast film which extended polymeric materials, although three-dimensions control of the refractive index in a phase contrast film is also important in an improvement of the angle-of-visibility property of a liquid crystal display and it is useful to angle-of-visibility expansion of a liquid crystal display that the optical axis leans, in order that a molecule may carry out orientation in the extension direction, it is substantially impossible to make an optical axis incline, and it becomes inadequate [ the effectiveness of angle-of-visibility expansion ]. Although the approach of irradiating photosensitive polymers, such as polyvinyl cinnamate, with polarization UV light at JP,7-138308,A is indicated as an approach of making phase contrast discovering by polarization exposure, since an anisotropy is discovered to electric-field vibration and perpendicularly of polarization UV light it

irradiated and an optical axis cannot be leaned, by this approach, it is hard to expand an angle of visibility. What carried out orientation immobilization of a liquid crystallinity macromolecule or the liquid crystallinity compound as an approach of solving the above-mentioned technical problem on the base material which carried out orientation processing is considered. Although the approach of making carry out orientation of the liquid crystallinity monomer, and fixing on the orientation film obtained [ SiO / a polarization exposure, rubbing processing, or ] by carrying out the method vacuum evaporation of slanting in UV light is proposed in JP,8-15681,A Since the orientation processing layer is prepared, the manufacturing cost of a phase contrast film which the process became [ manufacturing cost ] complicated and made the optical axis of a large area incline becomes high.

[0003]

[Problem(s) to be Solved by the Invention] When the optical compensation effect under an elevated temperature falls, in order that a molecule may carry out orientation of the phase contrast of the phase contrast film produced by the extension orientation of a high polymer film in the extension direction, it is remarkably difficult for it to make an optical axis incline. By the approach of on the other hand making a liquid crystallinity macromolecule and a liquid crystallinity compound arranging on the base material which carried out orientation processing, although it is possible to produce the phase contrast film which made the optical axis incline, since a process becomes complicated, the phase contrast film which made the optical axis of a large area incline by low cost cannot be obtained.

[0004]

[Means for Solving the Problem] By this invention, the phase contrast film which made arbitration discover big wavelength dispersion nature, the temperature-compensation effectiveness, and the direction of an optical axis is offered at the simple process of exposing the film of a photosensitive polymer and the mixture of a low molecular weight compound. By the manufacture approach (phase contrast film to twist) of the phase contrast film of this invention, a photosensitive polymer and the mixture of a low molecular weight compound are produced, and when orientation of the molecule in the film can be carried out by exposing this film, big wavelength dispersion nature and the temperature dependence of a birefringence can be given. If this exposure is performed from across to a film plane, since arbitration can be made to be able to incline and orientation of the optical axis can be carried out, big wavelength dispersion nature, the temperature-compensation effectiveness, and the phase contrast film that set up the optical axis towards desired are produced.

[0005]

[Embodiment of the Invention] Below, the detail of this invention is explained. The above-mentioned photosensitive polymer is a giant molecule which has a side chain including the structure which combined substituents, such as a biphenyl currently used abundantly as a meso gene component of a liquid crystallinity giant molecule, terphenyl, phenyl benzoate, and an azobenzene, and photosensitive radicals, such as a cinnamic acid radical (or the derivative radical), and has structures, such as a hydrocarbon, acrylate, methacrylate, maleimide, N-phenyl maleimide, and a siloxane, in a principal chain. It can become a phase contrast film with the wavelength dispersion nature of the transmitted light effective [ the film to which orientation of this ingredient was carried out since the ingredient containing meso gene components, such as such a biphenyl, was large ] in optical compensation. The spreading film (film) which applied this photosensitive polymer and the mixed solution of a low molecular weight compound on the base material (a spin coat or cast) is formed. This film is isotropy at the time of film production, and the photosensitive side-chain section and the photosensitive low molecular weight compound of a polymer have not turned to the specific direction. About the case where polarization exposure is carried out, this condition is explained based on drawing 2 . In the spreading film 20, low-molecular-weight-compound 2c shown with side-chain 2b and the cylinder of scarce arrangement of sensitization radical 2a shown with prolate ellipsoid, side-chain 2a of the photosensitive high arrangement which has 2b and is in the

sense corresponding to a perpendicular direction to the oscillating direction  $m$  and exposure Mitsuyuki line writing direction of the exposure polarization ultraviolet rays  $L$ , and photosensitivity lives together disorderly. If polarization exposure of this film is carried out, the photoreaction of side-chain 2a of the arrangement which is in the sense corresponding to a perpendicular direction to the electric-field oscillating direction and travelling direction of exposure light will advance preferentially. In order to advance this photoreaction, the exposure of the light of wavelength to which the part of a photosensitive radical can react is required. Although this wavelength changes also with classes of photosensitive radical, generally it is 200 to 500 nm, and its effectiveness of 250 to 400 nm is high especially in many cases.

[0006] Drawing 3 shows the film 30 after it carries out an optical exposure at the film of drawing 2 and a reaction advances. By the molecular motion after polarization exposure, as shown in drawing 3, reorientation of side-chain 3b (2b) and low-molecular-weight-compound 3c (2c) of a polymer which did not start the photoreaction is carried out. Namely, since it was not perpendicularly suitable to the both sides of the electric-field oscillating direction of polarization, and an exposure Mitsuyuki line writing direction, reorientation of side-chain 3b and low-molecular-weight-compound 3c of the polymer which did not start the photoreaction is carried out in the same direction as side-chain 3a (2a) which carried out the photoreaction. Consequently, in the whole spreading film, the side chain of a polymer and the molecule of a low molecular weight compound carry out orientation perpendicularly to the electric-field oscillating direction and exposure Mitsuyuki line writing direction of the linearly polarized light which were irradiated, induction of the birefringence is carried out, and it becomes the film which has the big phase contrast of wavelength dispersion. The directions differ in the time of polarization exposure and unpolarized light exposure. At the time of unpolarized light exposure, the photoreaction of the side chain of the arrangement which is in the sense corresponding to a perpendicular direction to the travelling direction of exposure light advances preferentially. By the molecular motion after exposure, the side chain of the polymer in the film and the molecule of a low molecular weight compound carry out orientation in the direction same since it arranged in parallel to the exposure Mitsuyuki line writing direction as the side chain of the polymer which did not start the photoreaction, induction of the birefringence is carried out and it serves as a phase contrast film. By performing this exposure from across to a film surface, arbitration can be made to be able to incline and orientation of the optical axis can be carried out. Consequently, the phase contrast film which set up the optical axis towards desired can be offered. measurement of the inclination of an optical axis -- Japanese Journal Applied Physics and Vol. -- the crystal rotation method which measures the transparency reinforcement of polarization was used, rotating the test portion indicated by 19 and 2013 (1980). By this measuring method, measurement of the three-dimensional birefringence of a test portion can be performed from the angular dependence of the permeability of polarization. The orientation by the molecular motion after exposure is promoted by heating a substrate. Whenever [ stoving temperature / of a substrate ] is lower than the softening temperature of the part which carried out the photoreaction, and it is desirable that it is higher than the softening temperature of the side chain which did not carry out the photoreaction, and a low molecular weight compound. Thus, if the film which exposes and carried out orientation under the film which it heated [ film ] and carried out orientation of the low molecular weight compound to the unreacted side chain, or heating is cooled below to the softening temperature temperature of this macromolecule after exposing, a molecule will carry out orientation. With the film which was exposed again and promoted bridge formation further behind the orientation by this molecular motion, it has the temperature dependence of a reversible birefringence. This is for orientation to happen along with the side chain or molecule currently fixed in the film according to bridge formation at the time of cooling, although relaxation of the molecular orientation in a film advances with heat. In the liquid crystal cell of the liquid crystal display of a STN mold, if the film which has the temperature dependence of this birefringence is used, relaxation of the orientation of the liquid crystal molecule produced by the temperature rise is followed, and

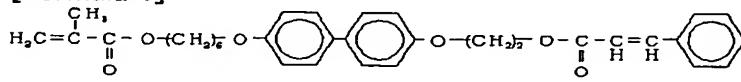
the fall of display properties, such as a color gap, can be controlled. Furthermore, the temperature dependence of a birefringence can be controlled by the phase contrast film of this invention by changing a polymer or the class of low molecular weight compound, and a thermal property, and temperature compensation is possible in various liquid crystal ingredients. When it has heat and/or photoreaction nature to low molecular weight compounds or this macromolecule, since orientation is fixed firmly, the low molecular weight compound mixed in this invention can expect heat-resistant improvement. In such a case, it is necessary to stop light exposure, or to adjust reactivity and to control the consistency of a photoreaction point not to bar the molecular motion at the time of the orientation after exposure.

[0007] While a low molecular weight compound has the effectiveness which will bloom cloudy if it is optimum dose, and controls whenever, if it adds superfluously, it will bloom cloudy, and causes the increment in whenever, and the fall of a stacking tendency. although based also on a photosensitive polymer or the class of low molecular weight compound from such a viewpoint -- a low molecular weight compound -- 0.1wt(s)% - 80wt% -- although a phase contrast film can be manufactured even if it adds, it is desirable that it is 5wt(s)% - 50wt% preferably. Here, when the compatibility of a polymer and a low molecular weight compound is not enough, the detailed crystal of sufficient magnitude to scatter about phase separation and the light with heating of the substrate after the time of film production or exposure is generated, and it becomes the cause of the increment in whenever [ cloudy ].

[0008] As the technique of thickening thickness and acquiring bigger phase contrast, the approach of carrying out the laminating of the film is mentioned. In this case, although the laminating of the ingredient solution is applied and carried out on the film which produced previously and was exposed, in order to prevent destruction of this film formed previously, it is effective to dissolve and use a polymer and a low molecular weight compound for the solvent which lowered solubility. Moreover, a birefringence comes to be more efficiently discovered by exposing from a front rear face on the film of a photosensitive polymer and the mixture of a low molecular weight compound. In this case, a photosensitive polymer and the mixture of a low molecular weight compound are applied on a base material, and are produced, and exposure may mind direct or a base material. In minding a base material, although what kind of ingredient is sufficient as a base material as long as it has the permeability of the light of wavelength to which a photosensitive polymer can react, there is so little light exposure that light transmittance is high, it ends, and becomes advantageous on a production process. Moreover, a polymer photosensitive in the base material top of detachability and the mixture of a low molecular weight compound can be produced, and it can also expose from a membranous front rear face after exfoliation.

[0009] The synthetic approach about the raw material compound of the photosensitive side-chain mold liquid crystallinity macromolecule used for the example of this invention is shown below. (Monomer 1) The 4-hydroxy-4'-hydroxy ethoxy biphenyl was compounded by heating 4, and 4'-biphenyl diol and 2-chloroethanol under alkali conditions. 1 and 6-dibromo hexane was made to react to this product under alkali conditions, and the 4-(6-BUROMO hexyloxy)-4'-hydroxy ethoxy biphenyl was compounded. Subsequently, lithium methacrylate was made to react and the 4-hydroxy ethoxy-4'-(6-methacryloyl hexyloxy) biphenyl was compounded. Finally, the phenylacrylyl chloride was added to the bottom of a basic condition, and the monomer 1 shown in a chemical formula 1 was compounded.

[Formula 1]



... (化学式1)

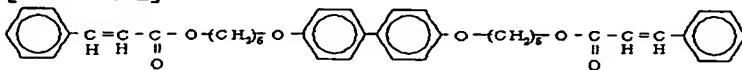
[0010] (Polymer 1) This monomer 1 was dissolved into the tetrahydrofuran and the polymer 1 was obtained by adding and carrying out the polymerization of the azobisisobutironitoriru

(azobisisobutyronitril) as a reaction initiator. This polymer 1 presented liquid crystallinity in the temperature field of 47 to 75 degree C.

[0011] (Polymer 2) This monomer 1 and stearyl methacrylate ester were dissolved into the tetrahydrofuran by the mole ratio of 0.85:0.15, and the polymer 2 was obtained by adding and carrying out the polymerization of the azobisisobutyronitril as a reaction initiator. This polymer 2 also presented liquid crystallinity.

[0012] (Low molecular weight compound 1) 4, and 4'-biphenyl diol and 6-BUROMO hexanol are made to react under alkali conditions, and they are 4 and 4'. – The screw (6-BUROMO hexyloxy) biphenyl was compounded. Subsequently, add a phenylacrylyl chloride, it was made to react to the bottom of a basic condition, and the low molecular weight compound 1 shown in a chemical formula 2 was compounded by carrying out column purification of the product.

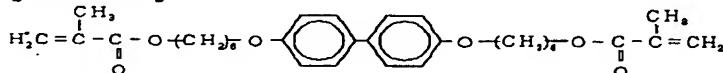
[Formula 2]



... (化学式2)

[0013] (Low molecular weight compound 2) 4, 4'-biphenyl diol and 1, and 6-dibromo hexane are made to react under alkali conditions, and they are 4 and 4'. – The screw (6-BUROMO hexyloxy) biphenyl was compounded. Subsequently, lithium methacrylate was made to react and the low molecular weight compound 2 shown in a chemical formula 3 was compounded by carrying out column purification of the product.

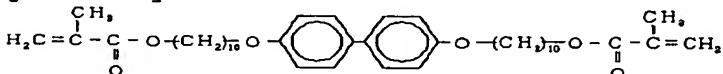
[Formula 3]



... (化学式3)

[0014] (Low molecular weight compound 3) 4, 4'-biphenyl diol and 1, and 6-dibromo decane are made to react under alkali conditions, and they are 4 and 4'. – Screw (6-BUROMO deca nil) The biphenyl was compounded. Subsequently, lithium methacrylate was made to react and the low molecular weight compound 3 shown in a chemical formula 4 was compounded by carrying out column purification of the product.

[Formula 4]



... (化学式4)

[0015]

[Example] The example of the manufacture approach (equipment) at the time of producing the phase contrast film of this invention by exposing the ultraviolet radiation of linearly polarized light nature is shown in drawing 1. However, the manufacture approach of the phase contrast film of this invention is not limited to this. The disorderly light 16 generated with the ultraviolet ray lamp 11 excited by the power source 12 has an optical element 13 (for example, the Gulan Taylor prism), is changed into the ultraviolet rays 17 of linearly polarized light nature, and irradiates the film 14 of the photosensitive polymer applied on the base material 15 (coat), and the mixture of a low molecular weight compound.

[0016] (Example 1) 3.75% of the weight of the polymer 1 and 1.25% of the weight of the low molecular weight compound 1 were dissolved in the dichloroethane, and it applied by the thickness of about 3 micrometers on the quartz substrate. The ultraviolet rays which leaned this substrate 45 degrees to the horizontal plane, have arranged so that a spreading side may turn into an exposure

side, irradiated perpendicularly the ultraviolet rays changed into the linearly polarized light using the Gulan Taylor prism two times 200 mJ/cm at the room temperature to the horizontal plane, then changed the substrate into the linearly polarized light inside out similarly were irradiated two times 200 mJ/cm. Next, after heating at 100 degrees C, it cooled to the room temperature. Thus, as for the obtained substrate, 67 degrees of optical axis leaned from [ of a substrate ] the normal, the phase contrast within a substrate side was 104nm, and whenever [ cloudy ] was what is not almost and can be equal to practical use enough. Moreover, when phase contrast within a field in t degrees C was made into Rtdegree C, it is R60 degree-C/R30 degree-C=0.88, R80 degree-C/R30 degree-C=0.29, R100 degree-C/R30 degree-C=0.08, and R120 degree-C/R30 degree-C=0.06, and the temperature dependence of phase contrast was checked. The birefringence temperature dependence of an example 1 is shown in drawing 4. Furthermore, the ratio (R400 nm/R550nm) of the phase contrast measured on the wavelength of 400nm and the phase contrast measured on the wavelength of 550nm is R400 nm/R550nm=1.23, and having big wavelength dispersion nature was checked.

[0017] (Example 2) 3.75% of the weight of the polymer 1 and 1.25% of the weight of the low molecular weight compound 2 were dissolved in the dichloroethane, and it applied by the thickness of about 3 micrometers on the quartz substrate. The ultraviolet rays which leaned this substrate 45 degrees to the horizontal plane, have arranged so that a spreading side may turn into an exposure side, irradiated perpendicularly the ultraviolet rays changed into the linearly polarized light using the Gulan Taylor prism two times 120 mJ/cm at the room temperature to the horizontal plane, then changed the substrate into the linearly polarized light inside out similarly were irradiated two times 120 mJ/cm. Next, after heating at 100 degrees C, it cooled to the room temperature. Thus, as for the obtained substrate, 67 degrees of optical axis leaned from [ of a substrate ] the normal, and the phase contrast within a substrate side was 238nm. Moreover, it is R60 degree-C/R30 degree-C=0.99, R80 degree-C/R30 degree-C=0.91, R100 degree-C/R30 degree-C=0.74, and R120 degree-C/R30 degree-C=0.44, and the temperature dependence of phase contrast was checked. Furthermore, it was R400 nm/R550nm=1.25.

[0018] (Example 3) 3.75% of the weight of the polymer 1 and 1.25% of the weight of the low molecular weight compound 3 were dissolved in the dichloroethane, and it applied by the thickness of about 3 micrometers on the quartz substrate. The ultraviolet rays which leaned this substrate 45 degrees to the horizontal plane, have arranged so that a spreading side may turn into an exposure side, irradiated perpendicularly the ultraviolet rays changed into the linearly polarized light using the Gulan Taylor prism two times 120 mJ/cm at the room temperature to the horizontal plane, then changed the substrate into the linearly polarized light inside out similarly were irradiated two times 120 mJ/cm. Next, after heating at 100 degrees C, it cooled to the room temperature. Thus, as for the obtained substrate, 67 degrees of optical axis leaned from [ of a substrate ] the normal, and the phase contrast within a substrate side was 65nm. Moreover, it is R60 degree-C/R30 degree-C=0.95, R80 degree-C/R30 degree-C=0.48, R100 degree-C/R30 degree-C=0.40, and R120 degree-C/R30 degree-C=0.30, and the temperature dependence of phase contrast was checked. Furthermore, it was R400 nm/R550nm=1.24.

[0019] (Example 4) 3.75% of the weight of the polymer 2 and 1.25% of the weight of the low molecular weight compound 1 were dissolved in the dichloroethane, and it applied by the thickness of about 3 micrometers on the quartz substrate. The ultraviolet rays which leaned this substrate 45 degrees to the horizontal plane, have arranged so that a spreading side may turn into an exposure side, irradiated perpendicularly the ultraviolet rays changed into the linearly polarized light using the Gulan Taylor prism two times 120 mJ/cm at the room temperature to the horizontal plane, then changed the substrate into the linearly polarized light inside out similarly were irradiated two times 120 mJ/cm. Next, after heating at 100 degrees C, it cooled to the room temperature. Thus, as for the obtained substrate, 67 degrees of optical axis leaned from [ of a substrate ] the normal, the phase contrast within a substrate side was 104nm, and whenever [ cloudy ] was what is not almost

and can be equal to practical use enough. Moreover, it is R60 degree-C/R30 degree-C=0.23, R80 degree-C/R30 degree-C=0.02, R100 degree-C/R30 degree-C=0.0, and R120 degree-C/R30 degree-C=0.0, and the temperature dependence of phase contrast was checked. Furthermore, it was R400 nm/R550nm=1.24.

[0020] (Example 5) 3.75% of the weight of the polymer 1 and 1.25% of the weight of the liquid crystal ingredient E7 (Merck Japan) were dissolved in the dichloroethane, and it applied by the thickness of about 3 micrometers on the quartz substrate. The ultraviolet rays which leaned this substrate 45 degrees to the horizontal plane, have arranged so that a spreading side may turn into an exposure side, irradiated perpendicularly the ultraviolet rays changed into the linearly polarized light using the Gulan Taylor prism two times 120 mJ/cm at the room temperature to the horizontal plane, then changed the substrate into the linearly polarized light inside out similarly were irradiated two times 120 mJ/cm. Next, after heating at 100 degrees C, it cooled to the room temperature. Thus, as for the obtained substrate, 67 degrees of opticals axis leaned from [ of a substrate ] the normal, and the phase contrast within a substrate side was 152nm. Moreover, it is R60 degree-C/R30 degree-C=0.99, R80 degree-C/R30 degree-C=0.94, R100 degree-C/R30 degree-C=0.92, and R120 degree-C/R30 degree-C=0.82, and the temperature dependence of phase contrast was checked. Furthermore, it was R400 nm/R550nm=1.24.

[0021] When the phase contrast which made big wavelength dispersion nature and the temperature-compensation effectiveness discover was able to be acquired from these examples by exposure, it has proved that the film which controlled the direction of an optical axis was producible.

[0022]

[Effect of the Invention] A photosensitive compound is film-ized, and by simple actuation of exposure, while being able to carry out orientation of the molecule in a film, big wavelength dispersion nature and the temperature dependence of a birefringence can be given to the transmitted light. Even if it does not use a conventional technique like an extension process according to this approach, when a phase contrast film can be obtained, an optical axis can also be leaned by exposing from across. Moreover, production of the field where opticals axis differ in the same substrate is also possible by changing the direction of radiation of ultraviolet rays. It can twist and the phase contrast film with which the optical axis inclined can be utilized as an optical compensation film for angle-of-visibility expansion in the liquid crystal display using rotatory-polarization mode and birefringence mode using a nematic liquid crystal. Although such [ conventionally ] a phase contrast film with which the optical axis inclined was unproducible by low cost in the large area, it became producible [ the film which has big wavelength dispersion nature and the temperature-compensation effectiveness to the transmitted light, and controlled the direction of an optical axis by simple actuation of exposing, by this invention ].

[0023]

---

[Translation done.]

\* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DESCRIPTION OF DRAWINGS

---

### [Brief Description of the Drawings]

[Drawing 1] The conceptual diagram showing the manufacture approach of the phase contrast film of this invention

[Drawing 2] The mimetic diagram of the side chain exposed by polarization exposure

[Drawing 3] The mimetic diagram of the side chain arranged by the molecular motion after polarization exposure

[Drawing 4] Temperature dependence of the phase contrast of an example 1

### [Description of Notations]

11 ... Ultraviolet ray lamp

12 ... Power source

13 ... Optical element (the Gulan Taylor prism)

14 ... Film (film)

15 ... Base material

16 ... Disorderly light

17 ... Ultraviolet rays of linearly polarized light nature

---

[Translation done.]

### \* NOTICES \*

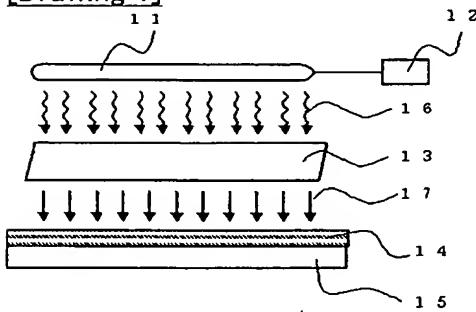
JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

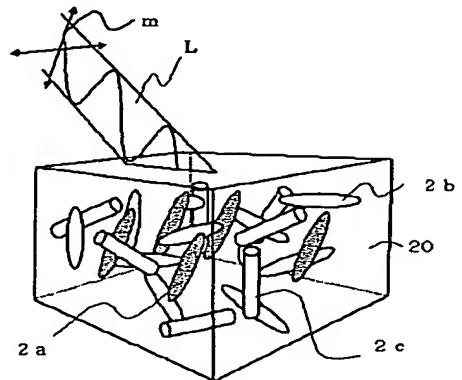
---

## DRAWINGS

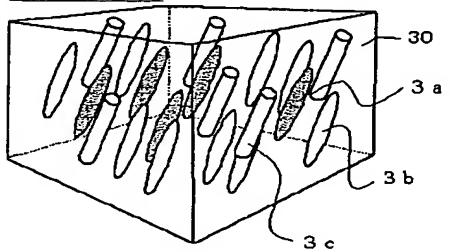
### [Drawing 1]



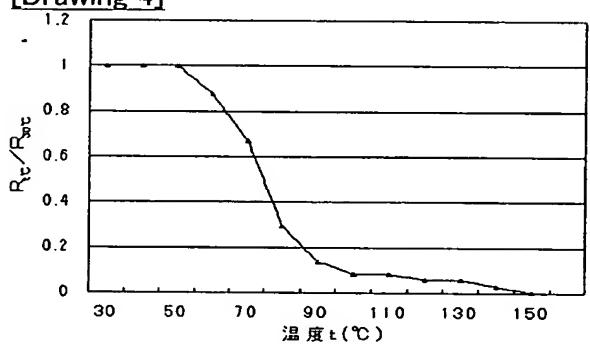
### [Drawing 2]



[Drawing 3]



[Drawing 4]



---

[Translation done.]

## 書誌

(19)【発行国】日本国特許庁(JP)  
(12)【公報種別】公開特許公報(A)  
(11)【公開番号】特開2002-202408(P2002-202408A)  
(43)【公開日】平成14年7月19日(2002. 7. 19)  
(54)【発明の名称】位相差フィルムおよびその製造方法  
(51)【国際特許分類第7版】

G02B 5/30  
G02F 1/13363

## 【FI】

G02B 5/30  
G02F 1/13363

【審査請求】未請求

【請求項の数】5

【出願形態】OL

【全頁数】6

(21)【出願番号】特願2000-400355(P2000-400355)

(22)【出願日】平成12年12月28日(2000. 12. 28)

(71)【出願人】

【識別番号】000251060

【氏名又は名称】林テレンプ株式会社

【住所又は居所】愛知県名古屋市中区上前津1丁目4番5号

(72)【発明者】

【氏名】酒井 丈也

【住所又は居所】愛知県名古屋市中区上前津1丁目4番5号林テレンプ株式会社内

(72)【発明者】

【氏名】植月 正雄

【住所又は居所】岡山県倉敷市酒津2545-5

(72)【発明者】

【氏名】川月 喜弘

【住所又は居所】兵庫県姫路市辻井4丁目7-31-8

【テーマコード(参考)】

2H049  
2H091

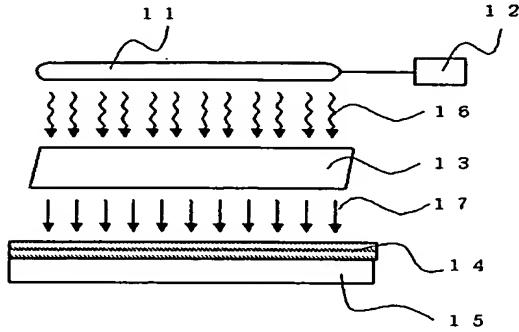
## 【Fターム(参考)】

2H049 BA06 BA42 BB42 BC01 BC05 BC22  
2H091 FA11X FA11Z FB02 FC22 FC23 LA12 LA19  
要約

## (57)【要約】

【目的】感光性の重合体と低分子化合物の混合体のフィルムを露光することによって分子配向させ、透過光に対して大きな波長分散性や温度補償効果を有し、光軸方向を制御した位相差フィルムおよび、その製造法の実現。

【構成】感光性の重合体と低分子化合物の混合体をフィルムにする。該フィルムを、紫外線ランプおよび電源、あるいは自然光を偏光に変換する光学素子(例えはグランテーラー・プリズム)からなる装置を用い露光し、特定方向に配置した感光性基の光反応を促進させると、透過光に対して大きな波長分散性や温度補償効果を有する位相差フィルムが得られる。この照射をフィルム面に対して斜め方向から行なうことによって、光軸を任意に傾斜させて配向させることができる。その結果、透過光に対して大きな波長分散性や温度補償効果を有すると共に、光軸を所望の方向に設定した位相差フィルムを提供できる。



## 請求の範囲

### 【特許請求の範囲】

【請求項1】感光性の重合体と低分子化合物の混合体のフィルムに光照射する操作を含む工程で作製されると共に、可視光の平均波長領域に関して30°Cでの位相差と80°Cにおける位相差の比( $R_{80^\circ\text{C}}/R_{30^\circ\text{C}}$ )が $0.01 < R_{80^\circ\text{C}}/R_{30^\circ\text{C}} < 0.97$ で、400nmの波長で測定した位相差と550nmの波長で測定した位相差の比( $R_{400\text{nm}}/R_{550\text{nm}}$ )が $1.15 < R_{400\text{nm}}/R_{550\text{nm}}$ であり、クリスタルローテーション法で測定される光軸の傾き( $\theta$ )が $0^\circ \leq \theta < 90^\circ$ であることを特徴とする位相差フィルムおよびその製造方法。

【請求項2】感光性の重合体と低分子化合物の混合体のフィルムに表裏面両方向から光照射する操作を含む工程で作製されることを特徴とする、請求項1の位相差フィルムおよびその製造方法。

【請求項3】支持体上に形成された感光性の重合体と低分子化合物の混合体のフィルムに表面および支持体を介して裏面の両方向から光照射する操作を含む工程で作製されることを特徴とする、請求項1の位相差フィルムおよびその製造方法。

【請求項4】請求項1、請求項2、および請求項3において照射する光が、直線偏光性または部分偏光性である位相差フィルムおよびその製造方法。

【請求項5】請求項1、請求項2、請求項3および請求項4に記載の位相差フィルムおよびその製造方法において、加熱、および／または冷却する工程を含むことを特徴とする位相差フィルムおよびその製造方法。

## 詳細な説明

### 【発明の詳細な説明】

#### 【0001】

【発明の属する技術分野】本発明は、感光性の重合体と低分子化合物の混合体の膜に、紫外線を照射する(以下、露光といふ)ことによって、分子配向させ、大きな波長分散性、温度補償効果および、光軸方向を任意に発現させた位相差フィルムおよび、その製造法に関するものである。(特に、光軸がフィルム面に対し傾いた位相差フィルムは液晶表示装置において視野角拡大に有効である。)

#### 【0002】

【従来の技術】STN型の液晶表示装置における白黒、又はカラー化では位相差フィルムが必要であ

る。この位相差フィルムは、互いに垂直な主軸方向に振動する直線偏光成分を通過させ、この二成分間に必要な位相差を与える複屈折を有するフィルムであり、STN型の液晶セルを透過してきたR、G、Bの楕円偏光の楕円率を減少させたり、R、G、Bの楕円偏光の主軸を一定方向に回転させ白黒、又はカラー化を可能にしている。このような位相差フィルムとして、ポリカーボネートなどの高分子材料を延伸し、高分子鎖を配向させ、延伸方向の屈折率と、延伸方向に対し直交方向の屈折率に差異を生じさせたものがある。しかしながら、高速応答性を要求される液晶表示装置では複屈折の大きな液晶材料が用いられるため液晶セルの波長分散性が大きくなり、これを補償するためにより波長分散性の大きな位相差フィルムが望まれている。また、温度上昇にともないSTN型液晶セルのレターデーションが変化するため、液晶表示装置を車載用として用いる場合、高温下で色ずれが生じ表示特性が低下する。これは、STN型の液晶表示装置の液晶セルでは温度の上昇により液晶分子の配向の緩和が生じるためである。これらの課題に対し、光学補償のために液晶セルを用いた、二層式STN型液晶表示装置が考えられるが、液晶表示装置の重量が増す、厚くなる、コストが高くなるなどの問題がある。ポリカーボネートなどの高分子材料を延伸した位相差フィルムでは、波長分散性が小さく光学補償効果が十分に得られない。波長分散性の大きい位相差フィルムとしては、ポリアリレート、ポリスルホン、ポリエーテルスルホン、芳香族ポリエスチル等の高分子材料を延伸した位相差フィルムが挙げられる。しかしながら、これらの高分子を配向させた位相差フィルムでは高温下での分子配向の緩和が小さく、室温で最も良好な表示特性を示すよう調整された液晶セルと位相差フィルムのレターデーションが高温下では最適条件から外れることにより、光学補償効果が十分に得られない。更に、液晶表示装置の視野角特性の改善において位相差フィルムにおける屈折率の三次元制御も重要であり、光軸が傾いていることが液晶表示装置の視野角拡大に役立つが、高分子材料を延伸した位相差フィルムでは、分子が延伸方向に配向するため、光軸を傾斜させることが実質的に不可能であり、視野角拡大の効果が不十分となる。偏光露光により位相差を発現させる方法として、特開平7-138308号にポリビニルシンナメートなどの感光性重合体を偏光UV光で照射する方法が記載されているが、該方法では照射した偏光UV光の電界振動と垂直方向に異方性が発現するため光軸を傾けることができないため視野角を拡大し難い。上記課題を解決する方法として、液晶性高分子や液晶性化合物を配向処理した基材上で配向固定したものも考えられ、特開平8-15681号ではUV光を偏光照射、ラビング処理もしくは、SiOを斜方蒸着して得られる配向膜上に液晶性モノマーを配向させ固定する方法が提案されているが、配向処理層を設けているため工程が煩雑となり大面積の光軸を傾斜させた位相差フィルムの製造費が高くなる。

#### 【0003】

【発明が解決しようとする課題】高分子フィルムの延伸配向によって作製された位相差フィルムの位相差は、高温下での光学補償効果が低下する上、分子が延伸方向に配向するため光軸を傾斜させることが著しく困難である。一方、配向処理した基材上で液晶性高分子や液晶性化合物を配列させる方法では、光軸を傾斜させた位相差フィルムを作製することは可能であるが、工程が煩雑となるため低コストで大面積の光軸を傾斜させた位相差フィルムを得ることはできない。

#### 【0004】

【課題を解決する手段】本発明では、感光性の重合体と低分子化合物の混合体の膜を露光するという簡便な工程で、大きな波長分散性、温度補償効果および、光軸方向を任意に発現させた位相差フィルムを提供する。本発明の位相差フィルムの製造方法(による位相差フィルム)では、感光性の重合体と低分子化合物の混合体を製膜し、該膜を露光することによって膜中の分子を配向させることができ、大きな波長分散性、複屈折の温度依存性を付与できる。この照射をフィルム面に対して斜め方向から行なうと、光軸を任意に傾斜させて配向させることができるので、大きな波長分散性、温度補償効果および、光軸を所望の方向に設定した位相差フィルムが作製される。

#### 【0005】

【発明の実施の形態】以下に、本発明の詳細を説明する。前述の感光性の重合体は、液晶性高分子のメソゲン成分として多用されているビフェニル、ターフェニル、フェニルベンゾエート、アゾベンゼンなどの置換基と、桂皮酸基(または、その誘導体基)などの感光性基を結合した構造を含む側鎖を有し、炭化水素、アクリレート、メタクリレート、マレイミド、N-フェニルマレイミド、シロキサンなどの構造を主鎖に有する高分子である。このようなビフェニルなどのメソゲン成分を含有する材料は透過光の波長分散性が大きいので、該材料を配向させたフィルムは光学補償に有効な位相差フィルムとなり

得る。該感光性の重合体と低分子化合物の混合溶液を基材上に塗布(スピンドルコートないしはキャスト)した塗布膜(フィルム)を形成する。該膜は、製膜時には等方性であり、感光性の重合体の側鎖部および低分子化合物は特定方向を向いていない。偏光露光した場合について、この状態を図2に基づいて説明する。塗布膜20中では、長楕円で示される感光基2a、2bを有し照射偏光紫外線Lの振動方向mかつ照射光進行方向に対し垂直方向に対応した向きにある感光性の高い配置の側鎖2aと感光性の乏しい配置の側鎖2bおよび円柱で示される低分子化合物2cが無秩序に共存している。該膜を偏光露光すると、照射光の電界振動方向かつ進行方向に対し垂直方向に対応した向きにある配置の側鎖2aの光反応が優先的に進行する。この光反応を進めるには、感光性基の部分が反応し得る波長の光の照射を要する。この波長は、感光性基の種類によっても異なるが、一般に200-500nmであり、中でも250-400nmの有効性が高い場合が多い。

【0006】図3は図2の膜に光照射して反応が進行した後の、膜30を示す。偏光露光後の分子運動により、図3に示すように、光反応を起こさなかった重合体の側鎖3b(2b)と低分子化合物3c(2c)は再配向する。即ち、偏光の電界振動方向と照射光進行方向の双方に対し垂直方向を向いていなかったため、光反応を起こさなかった重合体の側鎖3bと低分子化合物3cは、光反応した側鎖3a(2a)と同じ方向に再配向する。その結果、塗布膜全体において、照射した直線偏光の電界振動方向かつ照射光進行方向に対し垂直方向に重合体の側鎖と低分子化合物の分子が配向し、複屈折が誘起され、波長分散の大きな位相差を有するフィルムとなる。偏光露光時と非偏光露光時ではその方向が異なる。非偏光露光時には、照射光の進行方向に対し垂直方向に対応した向きにある配置の側鎖の光反応が優先的に進行する。露光後の分子運動により、照射光進行方向に対して平行方向に配置していたため、光反応を起こさなかった重合体の側鎖と同じ方向に膜中の重合体の側鎖と低分子化合物の分子が配向し、複屈折が誘起され位相差フィルムとなる。この露光を膜面に対して斜め方向から行なうことによって、光軸を任意に傾斜させて配向させることができる。その結果、光軸を所望の方向に設定した位相差フィルムを提供できる。光軸の傾斜の測定には、Japanese Journal Applied Physics, Vol. 19, 2013(1980)に記載された測定試料を回転させながら偏光の透過強度を測定するクリスタルローテーション法を用いた。該測定法では、偏光の透過率の角度依存性から測定試料の立体的な複屈折の測定ができる。露光後の分子運動による配向は、基板を加熱することにより促進される。基板の加熱温度は、光反応した部分の軟化点より低く、光反応しなかった側鎖と低分子化合物の軟化点より高いことが望ましい。このように露光したのち加熱し未反応側鎖と低分子化合物を配向させた膜または加熱下で露光し配向させた膜を該高分子の軟化点温度以下まで冷却すると分子が配向する。この分子運動による配向後、再度露光し更に架橋を促進したフィルムでは、可逆的な複屈折の温度依存性を有する。これは、熱によりフィルム中の分子配向の緩和が進行するものの、冷却時には架橋によってフィルム中に固定されている側鎖または分子に沿って配向が起こるためである。STN型の液晶表示装置の液晶セルにおいて、この複屈折の温度依存性を有するフィルムを用いると、温度上昇により生ずる液晶分子の配向の緩和に追従し、色ずれなどの表示特性の低下を抑制できる。更に、本発明の位相差フィルムでは、重合体もしくは低分子化合物の種類、熱的特性を変化させることにより、複屈折の温度依存性を制御でき、種々の液晶材料において温度補償が可能である。本発明において混合する低分子化合物は、低分子化合物同士、もしくは該高分子に対して熱および/または光反応性を有している場合には、配向が強固に固定されるため耐熱性の向上が期待できる。このような場合、露光後の配向時における分子運動を妨げないよう、露光量を抑えるか反応性を調整するなどして、光反応点の密度を制御する必要がある。

【0007】低分子化合物は、適量ならば曇り度を抑制する効果がある反面、過剰に添加すると曇り度の増加、配向性の低下を引き起す。このような観点から、感光性の重合体または低分子化合物の種類にもよるが、低分子化合物を0.1wt%~80wt%添加しても位相差フィルムは製造可能であるが、好ましくは5wt%~50wt%であることが望ましい。ここで、重合体と低分子化合物の相溶性が十分でない場合には、製膜時ないしは露光後の基板の加熱により相分離や可視光を散乱するのに十分な大きさの微細な結晶を生成し曇り度の増加の原因となる。

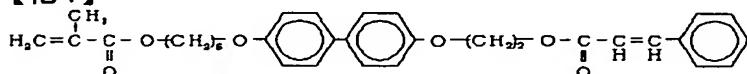
【0008】膜厚を厚くしより大きな位相差を得る手法として、膜を積層する方法が挙げられる。この場合、先に製膜し露光した膜上に材料溶液を塗布し積層するが、この先に形成された膜の破壊を防ぐために、溶解性を下げた溶媒に重合体および低分子化合物を溶解し用いることが有効である。また、感光性の重合体と低分子化合物の混合体の膜に表裏面から露光することによって、複屈折がより効

率よく発現するようになる。この場合、感光性の重合体と低分子化合物の混合体は支持体上に塗布するなどして製膜され、露光は膜面に直接または支持体を介してもよい。支持体を介する場合には、支持体は感光性の重合体の反応しうる波長の光の透過性を有している限りどのような材料でも良いが、光透過率が高い程、露光量が少なくて済み、製造工程上有利となる。また、剥離性の支持体上で感光性の重合体と低分子化合物の混合体を製膜し、剥離後、膜の表裏面より露光することもできる。

【0009】本発明の実施例に用いた感光性の側鎖型液晶性高分子の原料化合物に関する合成方法を以下に示す。

(単量体1)4, 4' - ビフェニルジオールと2-クロロエタノールを、アルカリ条件下で加熱することにより、4-ヒドロキシ-4' - ヒドロキシエトキシビフェニルを合成した。この生成物に、アルカリ条件下で1, 6-ジプロモヘキサンを反応させ、4-(6-プロモヘキシルオキシ)-4' - ヒドロキシエトキシビフェニルを合成した。次いで、リチウムメタクリレートを反応させ、4-ヒドロキシ-4' -(6-メタクリロイルヘキシルオキシ)ビフェニルを合成した。最後に、塩基性の条件下において、塩化シンナモイルを加え、化学式1に示される単量体1を合成した。

【化1】



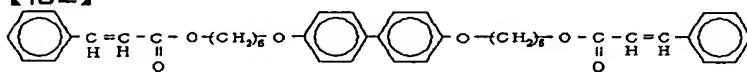
… (化学式1)

【0010】(重合体1)この単量体1をテトラヒドロフラン中に溶解し、反応開始剤としてAIBN(アゾビスイソブチロニトリル)を添加して重合することにより重合体1を得た。この重合体1は、47-75°Cの温度領域において、液晶性を呈した。

【0011】(重合体2)この単量体1とメタクリル酸ステアリルエステルとを0.85:0.15のモル比でテトラヒドロフラン中に溶解し、反応開始剤としてAIBNを添加して重合することにより重合体2を得た。この重合体2も液晶性を呈した。

【0012】(低分子化合物1)4, 4' - ビフェニルジオールと6-プロモヘキサノールを、アルカリ条件下で反応させ、4, 4' - ビス(6-プロモヘキシルオキシ)ビフェニルを合成した。次いで、塩基性の条件下において、塩化シンナモイルを加え反応させ、生成物をカラム精製することにより化学式2に示される低分子化合物1を合成した。

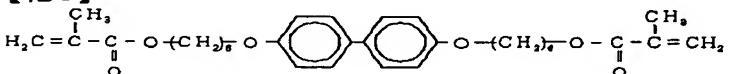
【化2】



… (化学式2)

【0013】(低分子化合物2)4, 4' - ビフェニルジオールと1, 6-ジプロモヘキサンを、アルカリ条件下で反応させ、4, 4' - ビス(6-プロモヘキシルオキシ)ビフェニルを合成した。次いで、リチウムメタクリレートを反応させ、生成物をカラム精製することにより化学式3に示される低分子化合物2を合成した。

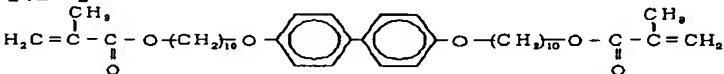
【化3】



… (化学式3)

【0014】(低分子化合物3)4, 4' - ビフェニルジオールと1, 6-ジプロモデカンを、アルカリ条件下で反応させ、4, 4' - ビス(6-プロモデカニル)ビフェニルを合成した。次いで、リチウムメタクリレートを反応させ、生成物をカラム精製することにより化学式4に示される低分子化合物3を合成した。

【化4】



… (化学式4)

## 【0015】

【実施例】図1には、本発明の位相差フィルムを直線偏光性の紫外光を露光することにより作製した場合の製造方法(装置)の例を示す。但し、本発明の位相差フィルムの製造方法はこれに限定されるものではない。電源12によって励起された紫外線ランプ11で発生した無秩序光16は、光学素子13(例えば、グランテーラープリズム)をもって直線偏光性の紫外線17に変換され、基材15上に塗布(コート)された感光性の重合体と低分子化合物の混合体の膜14を照射する。

【0016】(実施例1)3. 75重量%の重合体1および1. 25重量%の低分子化合物1をジクロロエタンに溶解し、石英基板上に約3μmの厚さで塗布した。該基板を水平面に対して45度傾け、塗布面が照射面となるように配置し、グランテーラープリズムを用いて直線偏光に変換した紫外線を、水平面に對し垂直方向から室温で200mJ/cm<sup>2</sup>照射し、続いて、基板を裏返し同様に直線偏光に変換した紫外線を200mJ/cm<sup>2</sup>照射した。次に、100°Cに加熱した後、室温まで冷却した。このようにして得られた基板は、光軸が基板の法線方向から67°傾いており、基板面内の位相差は104nmであり、曇り度は殆どなく実用に十分耐えうるものであった。また、t°Cにおける面内位相差をR<sub>t°C</sub>とすると、R<sub>60°C</sub>/R<sub>30°C</sub>=0. 88、R<sub>80°C</sub>/R<sub>30°C</sub>=0. 29、R<sub>100°C</sub>/R<sub>30°C</sub>=0. 08、R<sub>120°C</sub>/R<sub>30°C</sub>=0. 06であり位相差の温度依存性が確認された。図4に、実施例1の複屈折温度依存性を示す。更に、400nmの波長で測定した位相差と550nmの波長で測定した位相差の比(R<sub>400nm</sub>/R<sub>550nm</sub>)は、R<sub>400nm</sub>/R<sub>550nm</sub>=1. 23であり大きな波長分散性を有していることが確認された。

【0017】(実施例2)3. 75重量%の重合体1および1. 25重量%の低分子化合物2をジクロロエタンに溶解し、石英基板上に約3μmの厚さで塗布した。該基板を水平面に対して45度傾け、塗布面が照射面となるように配置し、グランテーラープリズムを用いて直線偏光に変換した紫外線を、水平面に對し垂直方向から室温で120mJ/cm<sup>2</sup>照射し、続いて、基板を裏返し同様に直線偏光に変換した紫外線を120mJ/cm<sup>2</sup>照射した。次に、100°Cに加熱した後、室温まで冷却した。このようにして得られた基板は、光軸が基板の法線方向から67°傾いており、基板面内の位相差は238nmであった。また、R<sub>60°C</sub>/R<sub>30°C</sub>=0. 99、R<sub>80°C</sub>/R<sub>30°C</sub>=0. 91、R<sub>100°C</sub>/R<sub>30°C</sub>=0. 74、R<sub>120°C</sub>/R<sub>30°C</sub>=0. 44であり位相差の温度依存性が確認された。更に、R<sub>400nm</sub>/R<sub>550nm</sub>=1. 25であった。

【0018】(実施例3)3. 75重量%の重合体1および1. 25重量%の低分子化合物3をジクロロエタンに溶解し、石英基板上に約3μmの厚さで塗布した。該基板を水平面に対して45度傾け、塗布面が照射面となるように配置し、グランテーラープリズムを用いて直線偏光に変換した紫外線を、水平面に對し垂直方向から室温で120mJ/cm<sup>2</sup>照射し、続いて、基板を裏返し同様に直線偏光に変換した紫外線を120mJ/cm<sup>2</sup>照射した。次に、100°Cに加熱した後、室温まで冷却した。このようにして得られた基板は、光軸が基板の法線方向から67°傾いており、基板面内の位相差は65nmであった。また、R<sub>60°C</sub>/R<sub>30°C</sub>=0. 95、R<sub>80°C</sub>/R<sub>30°C</sub>=0. 48、R<sub>100°C</sub>/R<sub>30°C</sub>=0. 40、R<sub>120°C</sub>/R<sub>30°C</sub>=0. 30であり位相差の温度依存性が確認された。更に、R<sub>400nm</sub>/R<sub>550nm</sub>=1. 24であった。

【0019】(実施例4)3. 75重量%の重合体2および1. 25重量%の低分子化合物1をジクロロエタンに溶解し、石英基板上に約3μmの厚さで塗布した。該基板を水平面に対して45度傾け、塗布面が照射面となるように配置し、グランテーラーパリズムを用いて直線偏光に変換した紫外線を、水平面に對し垂直方向から室温で120mJ/cm<sup>2</sup>照射し、続いて、基板を裏返し同様に直線偏光に変換した紫外線を120mJ/cm<sup>2</sup>照射した。次に、100°Cに加熱した後、室温まで冷却した。このようにして得られた基板は、光軸が基板の法線方向から67°傾いており、基板面内の位相差は104nmであり、曇り度は殆どなく実用に十分耐えうるものであった。また、R<sub>60°C</sub>/R<sub>30°C</sub>=0. 23、R<sub>80°C</sub>/R<sub>30°C</sub>=0. 02、R<sub>100°C</sub>/R<sub>30°C</sub>=0. 0、R<sub>120°C</sub>/R<sub>30°C</sub>=0. 0であり位相差の温度依存性が確認された。更に、R<sub>400nm</sub>/R<sub>550nm</sub>=1. 24であった。

【0020】(実施例5) 3.75重量%の重合体1および1.25重量%の液晶材料E7(メルクジャパン)をジクロロエタンに溶解し、石英基板上に約3μmの厚さで塗布した。該基板を水平面に対して45度傾け、塗布面が照射面となるように配置し、グランテーラーブリズムを用いて直線偏光に変換した紫外線を、水平面に対し垂直方向から室温で120mJ/cm<sup>2</sup>照射し、続いて、基板を裏返し同様に直線偏光に変換した紫外線を120mJ/cm<sup>2</sup>照射した。次に、100°Cに加熱した後、室温まで冷却した。このようにして得られた基板は、光軸が基板の法線方向から67°傾いており、基板面内の位相差は152nmであった。また、 $R_{60^\circ\text{C}}/R_{30^\circ\text{C}}=0.99$ 、 $R_{80^\circ\text{C}}/R_{30^\circ\text{C}}=0.94$ 、 $R_{100^\circ\text{C}}/R_{30^\circ\text{C}}=0.92$ 、 $R_{120^\circ\text{C}}/R_{30^\circ\text{C}}=0.82$ であり位相差の温度依存性が確認された。更に、 $R_{400\text{nm}}/R_{550\text{nm}}=1.24$ であった。

【0021】これらの実施例から、露光により、大きな波長分散性、温度補償効果を発現させた位相差を得られる上、光軸方向を制御したフィルムを作製でき立証できた。

#### 【0022】

【発明の効果】感光性の化合物をフィルム化し、露光という簡便な操作により、フィルム中の分子を配向させることができると共に、透過光に対して大きな波長分散性と複屈折の温度依存性を付与することができる。本方法によれば延伸工程のような従来技術を用いなくても位相差フィルムを得ることができると、斜め方向から露光することにより光軸を傾けることができる。また、紫外線の照射方向を変えることにより、同一基板内において、光軸の異なる領域の作製も可能である。光軸の傾斜した位相差フィルムは、旋光モード、複屈折モードを利用したねじれネマチック液晶を使った液晶表示装置において視野角拡大用の光学補償フィルムとして活用できる。従来このような、光軸の傾斜した位相差フィルムを大面積において低成本で作製することができなかつたが、本発明によって、露光するという簡便な操作で、透過光に対して大きな波長分散性や温度補償効果を有し、光軸方向を制御したフィルムの作製が可能となつた。

#### 【0023】

### 図の説明

#### 【図面の簡単な説明】

【図1】本発明の位相差フィルムの製造方法を示す概念図

【図2】偏光露光により感光した側鎖の模式図

【図3】偏光露光後の分子運動により配列した側鎖の模式図

【図4】実施例1の位相差の温度依存性

#### 【符号の説明】

11…紫外線ランプ

12…電源

13…光学素子(グランテーラーブリズム)

14…膜(フィルム)

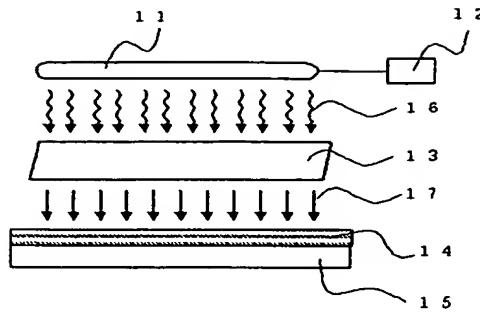
15…基材

16…無秩序光

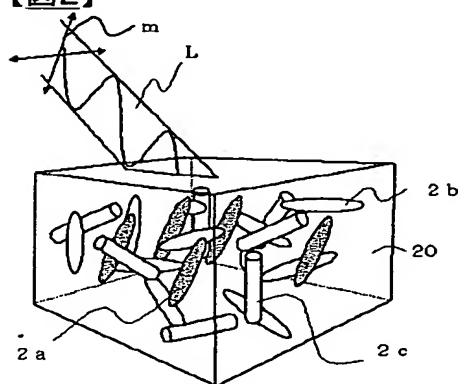
17…直線偏光性の紫外線

### 図面

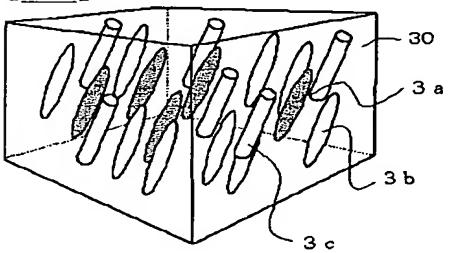
#### 【図1】



【図2】



【図3】



【図4】

